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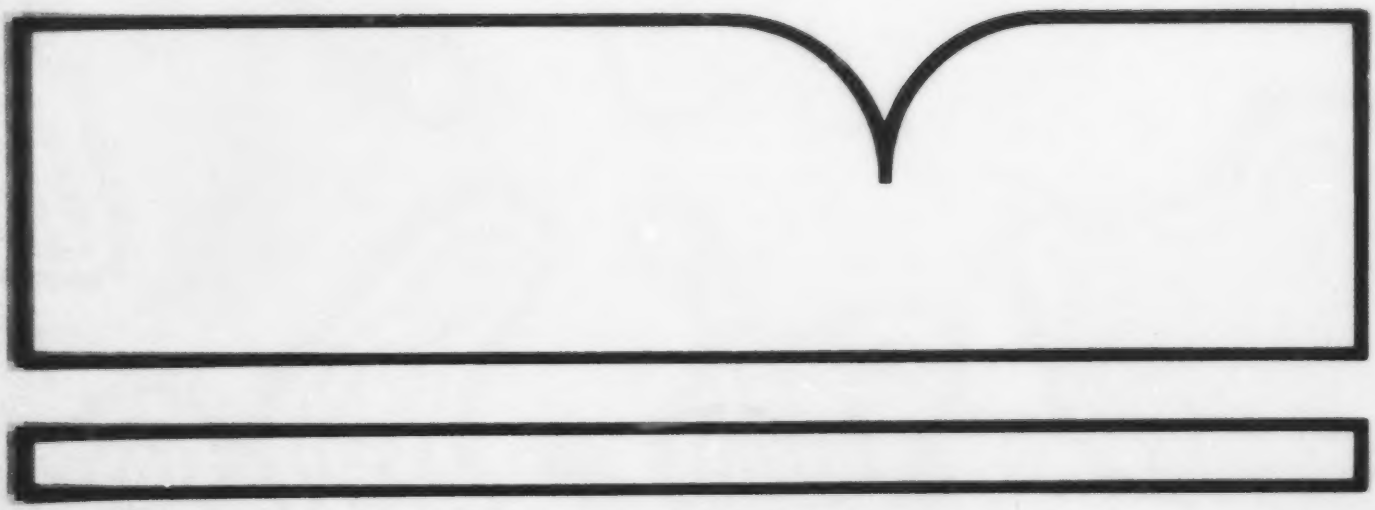

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16. ABSTRACT

An important, often primary, mechanism of chemical transformation of organic pollutants in the atmosphere is thru oxidation by OH radicals. The University of California-Riverside, Statewide Air Pollution Research Center, has developed a relatively simple laboratory procedure for determining the OH rate constants in air. To determine the rate, a Teflon bag is filled with 10-15 ppm of methyl nitrite, 5 ppm of nitric oxide, 2 ppm of test compound and 2 ppm of an organic which has an accurately known OH rate constant. The mixture is irradiated with blacklamps ($\lambda_{max} \sim 360$ nm) and the concentrations of the reference and test organic are measured over a 45-minute period. Regression analysis is performed to determine the ratio of $k_{OH\text{-test}}/k_{OH\text{-reference}}$ (the slope) where $X = (t-t_o)^{-1} \ln [(\text{Reference})_{t_o}/(\text{Reference})_t]$ and $y = (t-t_o)^{-1} \ln [(\text{test})_{t_o}/(\text{test})_t]$. Results obtained are acetylene $k_{OH} = (7.5 \pm 1.8) \times 10^{-13}$ cm^3 molec^{-1} s^{-1}, ethylene dichloride (tentative) $k_{OH} = (1.6 \pm 0.4) \times 10^{-13}$ cm^3 molec^{-1} s^{-1}, ethylene dibromide (tentative) $k_{OH} = (2.8 \pm 0.7) \times 10^{-13}$ cm^3 molec^{-1} s^{-1}, p-dichlorobenzene $k_{OH} = (4.2 \pm 0.9) \times 10^{-13}$ cm^3 molec^{-1} s^{-1} and carbon disulfide $k_{OH} = (3.0 \pm 0.6) \times 10^{-12}$ cm^3 molec^{-1} s^{-1}. We were unable to obtain a rate for nitrobenzene.

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INTRODUCTION

An important, often primary, mechanism of chemical transformation of organic pollutants in the atmosphere is thru oxidation by OH radicals. Knowledge of their rates of reaction with OH along with photolytic rates, their rates of reaction with O_3, O, NO_3, and removal from the gas phase by heterogeneous processes all are needed to evaluate the tropospheric fate of these chemicals. The organic-OH rate constant has also been identified as a key indicator of the potential for those organics to contribute to photochemical oxidant production.

The U.S. Environmental Protection Agency has determined that organics with OH rate constants less than or equal to that of ethane shall be considered 'non-reactive' for purposes of regulatory control with regards to the control of photochemically produced ozone.

The Office of Air Quality Planning and Standards (OAQPS) has identified six organics which have published OH rate constants near that of ethane. In some cases published rates for specific compounds have been found both above and below that of ethane. Therefore, it is not clear whether these chemicals should be classified as 'reactive' or 'non-reactive' for purposes of ozone control strategies. This study was undertaken to determine the rates of reaction of these compounds with OH relative to that of ethane.

The six compounds evaluated were: acetylene (C_2H_2), ethylene dichloride ($CClH_2CClH_2$), ethylene dibromide ($CBrH_2CBRH_2$), nitrobenzene ($C_6H_5NO_3$), p-dichlorobenzene ($p\text{-}ClC_6H_4Cl$), and carbon disulfide (CS_2). All but carbon disulfide have recently been reviewed for their OH reactivity by Atkinson[1]. We will not attempt to report this current and comprehensive review here. We will, however, summarize the findings of Atkinson with respect to those five compounds. The reader is referred to the review for an in-depth analysis of published rate constants of interest.

Acetylene

The rate of OH attack on acetylene has been found to be pressure dependent. At higher pressures (above 200-1000 Torr of N_2 or A_r) the energy rich adduct formed by

$$OH + C_2H_2 \rightarrow [HOCH = CH]^*$$

is stabilized by collision thus preventing decomposition to yield the initial OH and acetylene. Hence for atmospheric pressures Atkinson recommends

$$K_{C_2H_2} = 7.8 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \ (\pm 25\%) \text{ at } 298°K$$

The value of K_{OH} for ethane is recommended to be $K_{C_2H_6} = 2.74 \times 10^{-13}$ cm^3 $molec^{-1}$ s^{-1} at 298°K (± 20%).

Thus it appears that acetylene is about 2.85 times faster than ethane with respect to OH attack at 298°K and 760 mm. However, in consideration of the weight this determination may carry in terms of air quality and regulatory costs it was included for re-evaluation.

Ethylene dichloride (1,2-dichloroethane)

Atkinson found only one published rate constant for the OH-ethylene dichloride reaction. It is (2.20 ± 0.50) X 10^{-13} cm^3 $molec^{-1}$ s^{-1} at 296°K. Thus ethylene dichloride appears to be less reactive than ethane but was deemed to be sufficiently close to include for evaluation.

Ethylene dibromide

From the same work as ethylene dichloride Atkinson again found only one published value for ethylene dibromide. It is (2.50 ± 0.55) X 10^{-13} cm^3 $molec^{-1}$ s^{-1} at 296°K. It too was included for its close proximity to ethane.

Nitrobenzene

Atkinson found only one published rate determination for nitrobenzene. It is 1.33 X 10^{-13} cm^3 $molec^{-1}$ s^{-1} at 296°K.

P-dichlorobenzene

Only one published value was found for p-dichlorobenzene. It is (3.2 ± 0.2) X 10^{-13} cm^3 $molec^{-1}$ s^{-1} at 295°K.

Carbon disulfide

A review of recent papers concerning the OH - CS_2 reaction suggests that early studies disagreed because of oxygen effects and the UV absorption of CS_2 (see Jones et al.[2] and Barnes et al.[3]). The most recent studies[2-4] conducted at atmospheric pressure in the presence of oxygen suggest the rate is between 1.7 to 2.7 X 10^{-12} cm^3 $molec^{-1}$ s^{-1}.

EXPERIMENTAL SECTION

Hydroxyl radicals were generated by the photolysis of methyl nitrite in air:

$$CH_3ONO + h\nu \rightarrow CH_3O + NO \quad (1)$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2 \quad (2)$$

$$HO_2 + NO \rightarrow OH + NO_2 \quad (3)$$

In a typical irradiation a 100 ℓ, 2 mil FEP Teflon bag is charged with 10-15 ppm of CH_3ONO, 5 ppm of NO, and 2 ppm each of test compound and ethane. The mixture is irradiated with ultraviolet radiation ($\lambda > 300$ nm) and the concentrations of the hydrocarbons are measured over a 45 minute period[5-6].

The irradiation apparatus consisted of a temperature controlled 0.78m (W) x 1.35 m (l) x 1.12 m (Ht) aluminum box which contained two banks of twelve 40W fluorescent ultraviolet blacklamps. Two 100 ℓ Teflon bags were irradiated simultaneously. Monitoring of the contents of both bags was accomplished by alternately switching the common instrument manifold sampling line thru a 3-way Teflon solenoid valve. The manifold was used to supply samples to the gas chromatograph, Bendix chemiluminescence O_3 monitor, and Monitor Labs chemiluminescence NO_x analyzer. A Perkin Elmer 900 gas chromatograph equipped with flame ionization and flame photometric detection was used along with a Hewlett Packard 3390 Integrator to measure the test compound and ethane. A Porapak Q (60/80 mesh) column (3.2mm o.d. X 2.4m ss) and/or a 30 m DB-1 Megabore column (J&W Scientific) was used to separate both hydrocarbons. A Hewlett Packard 5880 Gas chromatograph equipped with flame ionization detection and a 30 m DB5 Megabore (1.5 μ film) column was used to analyze for nitrobenzene and p-dichlorobenzene. Sample injection was controlled by a solenoid actuated diaphragm type Seiscor gas sampling valve (Seismograph Co., Tulsa, OK). The value was heated to 90°C for the nitrobenzene and p-dichlorobenzene experiments. Bag valve switching, sample loading, sample injection, and integrator actuation were controlled by a ChronTrol timer (Lindberg Enterprises, San Diego, CA) such that GC injection was performed automatically every five minutes.

The Perkin Elmer flame ionization detector was replaced with a flame photometric detector (FPD) for the carbon disulfide determination. Also a 2.4m x 3/2mm o.d. FEP Teflon tube was packed with Chromosil 310 to separate CS_2, SO_2, and OCS.

Teflon bags were fabricated from 2 mil Type A fluorinated ethylene-propylene co-polymer (FEP) film using a thermal impulse heat sealer (Vertrod, Brooklyn, NY). All Teflon (TFE) ports were inserted in bags. Ultraclean air was produced by passing outside air through a heated (600°C) rhodium on aluminum catalyst (Engelhard), a series of traps (silica gel, Purafil-Borg Warner to remove NO_x and activated charcoal), a particle filter, a 3-way Teflon solenoid valve, and a rotameter. Test compounds and ethane (C.P. Grade, Matheson Gas Products) were introduced into the bag by syringe injection thru a glass T (with septum) placed in-line with the air train and bag. P-dichlorobenzene was introduced into the bag by passing diluent air through a glass sampling bulb (500 cc) which has been equilibrated with solid p-dichlorobenzene at room temperature. Methyl nitrite was prepared by the dropwise addition of 50% H_2SO_4 to sodium nitrite saturated methanol and purified according to the procedure described by Pitts et al.[5] Methyl nitrite and nitric oxide (C. P. grade, National Specialty Gases) were then injected into the bag under subdued light (to minimize photolysis of the methyl nitrite). Acetylene was prepared by dropwise addition of water to calcium carbide; impurities (i.e. NH_3, PH_3, H_2S) were removed by passing the gas stream thru traps of Purafil and Ascarite.

RESULTS

Irradiations of CH_3ONO-NO-test organic-ethane-air mixtures were carried out at 297 $\pm$ 4°K, with ethane being used as the reference organic.

Both organics react with OH radicals:

$$OH + \text{test compound} \rightarrow \text{products} \quad (4)$$

$$OH + \text{reference compound} \rightarrow \text{products} \quad (5)$$

Also the test organic may react with ozone and/or NO_3, or it may photolyze:

$$\text{test compound} + h\nu \rightarrow \text{products} \quad (6)$$

$$\text{test compound} + O_3 \rightarrow \text{products} \quad (7)$$

$$\text{test compound} + NO_3 \rightarrow \text{products} \quad (8)$$

Since NO is present in excess reactions 7 and 8 become negligible. The reference organic (ethane) does not photolyze or react significantly with O_3 or NO_3 under these conditions. If the rate of OH reaction with the reference compound is known then k_4 the OH reaction rate for the test compound can be evaluated by least squares fit of the data to the linear form:

$$\frac{1}{(t-t_o)} \ln \frac{(\text{test compound})_{to}}{(\text{test compound})_t} = K_6 + \frac{k_4}{k_5\,(t-t_o)} \ln \frac{(\text{reference compound})_{to}}{(\text{reference compound})_t} \quad (I)$$

The data is plotted where the left hand expression is the ordinate and $(t-t_o)^{-1} \ln [(\text{reference compound})_{to}/\text{reference compound})_t]$ is the abscissa. The slope is k_4/k_5 and k_6 (photolysis, wall loss or other competing processes) is the intercept.

Tabulations of regression analyses for each compound are found in the in Tables II-V. A brief summary of the results of all six compounds is found in Table I.

Acetylene

The average k_{OH} value obtained for acetylene was $(7.5 \pm 1.8) \times 10^{-13}$ cm^3 $molec^{-1}$ s^{-1}, this is in excellent agreement with Atkinson's[1] recommended value of $(7.8 \pm 1.9) \times 10^{-13}$ cm^3 $molec^{-1}$ s^{-1}. All intercepts were not statistically distinguishable from the origin at the 0.05 probability level; therefore, there did not appear to be any photolysis or competing non-OH removal processes operating. Our experiments did not show evidence of 'heterogeneous, first order light-induced decay of acetylene' seen by Atkinson and Aschmann in Teflon bags used more than once[7].

Ethylene dichloride

The average value obtained for ethylene dichloride was $(1.6 \pm 0.4) \times 10^{-13}$ cm^3 $molec^{-1}$ s^{-1}; this in good agreement with Atkinson's[1] recommended value of $(2.2 \pm 0.5) \times 10^{-13}$ cm^3 $molec^{-1}$ s^{-1}. However, the presence of chlorine in the molecule could cause the rate constant found to be biased

low if the chlorine is released and contributes to chains as described by Edney et al.[6] This can be checked by increasing the ethane to ethylene dichloride ratio and examining the effect upon the rate constant. If free chlorine is important the rate constant will increase with increasing ethane. Other removal processes such as photolysis and wall loss did not appear to be important as evidenced by the intercepts which are statistically indistinguishable from the origin. Experiments are in progress to determine if chlorine chemistry is interferring with the OH rate determination.

Ethylene dibromide

The average value obtained for ethylene dibromide was $(2.8 \pm 0.7) \times 10^{-13}$ cm^3 $molec^{-1}$ s^{-1}; this is in excellent agreement with Atkinson's recommended value of $(2.5 \pm 0.6) \times 10^{-13}$ cm^3 $molec^{-1}$ s^{-1}. However, it is again possible that bromine chemistry could cause the rate constant obtained to be biased low if free bromine is released. Additional experiments are being conducted at high ethane/ethylene dibromide ratios to determine if bromine chains are influencing the OH rate determination.

Nitrobenzene

We were unable to extract a statistically significant rate constant from the regression of nitrobenzene vs ethane. The slope of equation (I) was not significantly different from 0 (Student's t-test, 5% level of significance). The analytical precision for nitrobenzene was $\pm$ 2.0% good, but not as precise as those for most of the other compounds. Nitrobenzene with its low vapor pressure and polar nature contributed to adsorption on the sample lines and gc valving thus making reproducible injections less precise. In addition nitrobenzene had the lowest reported[1] rate constant of the six compounds 1.33×10^{-13} cm^3 $molec^{-1}$ s^{-1}. Based on our results, the rate must be less than 4×10^{-13} cm^3 $molec^{-1}$ s^{-1}.

Para-dichlorobenzene

The average value obtained for PDB was $(4.2 \pm 0.9) \times 10^{-13}$ cm^3 $molec^{-1}$ s^{-1}; this is in good agreement with the single literature value reported by Atkinson[1] of $(3.2 \pm 0.2) \times 10^{-13}$ cm^3 $molec^{-1}$ s^{-1}. To test for the possible influence of chlorine chains competing with the OH four runs were made with an ethane to PDB ratio of 16:1. If chlorine chains are significant relative to the OH attack then the measured rate constant should increase when the ethane is present in excess[6]. We observed about a 26% increase in the rate at the 16:1 ratio relative to the 1:1 ratio. This is a slight but statistically significant increase at the 95% confidence level. It appears that chlorine chains could be exerting a small influence on this rate determination. More data collected over a wider range of ethane/PDB ratios should be obtained to ascertain the extent of this effect.

Carbon disulfide

The average value obtained for CS_2 was $(3.0 \pm 0.6) \times 10^{-12}$ cm^3 $molec^{-1}$ s^{-1}; this is in fair agreement with the recently reported rate constants at atmospheric pressure in the presence of oxygen[2-4]. These are

Jones et al.[2] $(2.0 \pm 1.0) \times 10^{-12}$ cm^3 $molec^{-1}$ s^{-1}, Jones et al.[4] $(1.7 \pm 0.9) \times 10^{-12}$ cm^3 $mole^{-1}$ s^{-1} and Barnes et al.[3] $(2.7 \pm 0.6) \times 10^{-12}$ cm^3 $molec^{-1}$ s^{-1}. Recent studies[8] at low pressure in O_2 free systems showed the CS_2 + OH reaction to have an upper limit of around 1×10^{-14} cm^3 $molec^{-1}$ s^{-1}. Jones et al.[2] found that the rate increased with increasing pressure in the presence of sufficient O_2. They proposed that OH attack on CS_2 leads to the formation of an energy rich adduct which could subsequently react with oxygen or decompose:

$$OH + CS_2 \ (+M) \rightarrow CS_2OH \ (+M) \qquad (9)$$

and $$CS_2OH + O_2 \rightarrow OCS + SO_2 \qquad (10)$$

This mechanism is supported by the work of Barnes et al.[3] who found that the OH-CS_2 rate increased with increasing pressure, decreased with increasing temperature and increased with increasing oxygen. They also found that OCS and SO_2 were produced in equivalent quantitites. We also observed the co-production of OCS and SO_2.

In all of our experiments we observed a statistically significant positive y intercept. As shown in equation I this indicates a non-OH reaction competing for removal of the CS_2 i.e. photolysis. Barnes et al.[3] using the methyl nitrite photolysis procedure make no mention of any competing reactions. However, Jones et al.[2] found that CS_2 irradiated in air using either all blacklamps or a blacklamp/sunlamp combination led to production of OCS. Wood and Heicklen[10] irradiated CS_2 in the presence of O_2 and proposed the following mechanism based on their product analysis:

$$CS_2 + h\nu \ (313 \text{ nm}) \rightarrow CS_2^* \qquad (11)$$

$$CS_2^* + O_2 \rightarrow CS_2 + O_2 \qquad (12)$$

$$\rightarrow CS + SO_2 \qquad (13)$$

Jones et al.[2] propose that the CS react quantitatively under their conditions to produce OCS.

$$CS + O_2 \rightarrow OCS + O\cdot \qquad (14)$$

In summary it appears that the methyl nitrite relative rate method yields a rate close to other published rates using different methods. There does appear to be a competing non-OH process or processes for consumption of the CS_2 but its effect is recognized and does not influence the OH rate determination.

CONCLUSIONS

1. Acetylene. A value of $(7.5 \pm 1.8) \times 10^{-13}$ cm^3 $molec^{-1}$ s^{-1} was obtained using the methyl nitrite relative rate method with ethane as a reference compound. This is in excellent agreement with recent atmospheric pressure rates recently reviewed by Atkinson $(7.8 \pm 1.9) \times 10^{-13}$ cm^3 $molec^{-1}$ s^{-1}.

2. Ethylene dichloride. A value of $(1.6 \pm 0.4) \times 10^{-13}$ cm^3 $molec^{-1}$ s^{-1} was obtained for ethylene dichloride. If there is free chlorine in the system, this value could be a lower limit. Atkinson recommended a value of $(2.2 \pm 0.5) \times 10^{-13}$ cm^3 $molec^{-1}$ s^{-1} which is 38% higher than we obtained. We plan to perform a few additional experiments to determine if chlorine chemistry is important in this system.

3. Ethylene dibromide. A value of $(2.8 \pm 0.7) \times 10^{-13}$ cm^3 $molec^{-1}$ s^{-1} was obtained for ethylene dibromide. Again if free bromine is present in the system, bromine chains could influence the determination of the OH rate constant and the value obtained could be a lower limit for this rate constant. Atkinson recommended a value of $(2.5 \pm 0.6) \times 10^{-13}$ cm^3 $molec^{-1}$ s^{-1} for EDB. A few additional experiments are planned to evaluate the significance of bromine chemistry.

4. Nitrobenzene. We were unable to obtain a rate constant for nitrobenzene due to its apparent low value and less than required analytical precision. Atkinson's single reference to the nitrobenzene rate is 1.33×10^{-13} cm^3 $molec^{-1}$ s^{-1} which is the lowest reported value of the six compounds we evaluated in this study. Our analytical precision was only $\pm$ 2.0% for nitrobenzene which is generally considered good for gas analysis by gas chromatography. However, we were able to obtain $\pm$ 0.5% precision on many of our analyses for the other compounds in this study.

5. Para-dichlorobenzene. A value of $(4.2 \pm 0.9) \times 10^{-13}$ cm^3 $molec^{-1}$ s^{-1} was obtained for p-dichlorobenzene. This is about 30% higher than the value recommended by Atkinson $(3.2 \pm 0.2) \times 10^{-13}$ cm^3 $molec^{-1}$ s^{-1}. There was indication that there was competing chlorine chemistry as evidenced by a 26% increase in the rate when we changed the ethane: PDB ratio from 1:1 to 16:1.

6. Carbon disulfide. A value of $(3.0 \pm 0.6) \times 10^{-12}$ cm^3 $molec^{-1}$ s^{-1} was obtained for carbon disulfide. This is about 11% higher than reported by Barnes et al.[3] who used the same technqiue used in this work, 50% higher than Jones et al.[2] who used photolysis of HONO to generate OH. We varied the ethane: CS_2 ratio from 16:1 to 1:10. At the 1:10 ratio a rate about 58% lower than that obtained at ratios between 1:1 to 16:1 was observed. In addition we observed a significant y intercept in all of our $(t-t_o)^{-1}$ ln $[(CS_2)_o/(CS_2)_t]$ vs $(t-t_o)^{-1}$ ln $[(ethane)_o/(ethane)_t]$ plots. This indicates there is a competing removal process for CS_2; however, this should not influence the determination of the OH rate constant for CS_2. Note: Wall loss was evaluated and found to be insignificant.

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Table I. Summary of results.

Compound	Ethane / Test compound Ratio	Average* k_{OH} (± S.E) X 10^{13} cm^3 $molec^{-1}s^{-1}$	Average R^2 (%)	Atkinson[a] Recommended K_{OH} (± S.E.) X 10^{13} cm^3 $molec^{-1}$ s^{-1}
Acetylene	1:1	7.5 ± 1.8	96.5	7.8 ± 1.9
Ethylene Dichloride	1:1	1.6 ± 0.4	92.8	2.2 ± 0.5
Ethylene Dibromide	1:1	2.8 ± 0.7	90.1	2.5 ± 0.6
p-dichlorobenzene	1:1	3.9 ± 0.9	89.1	3.2 ± 0.2
	16:1	4.9 ± 1.1	93.0	
Carbon disulfide	1:10	12.7 ± 4.9	95.4	20. ± 10[b]
	1:1	28.5 ± 5.9	96.7	17 ± 9[c]
	8:1	26.5 ± 5.4	99.1	27 ± 6[d]
	16:1	35.9 ± 7.4	98.8	

* Assumes $K_{OH\text{-ethane}} = (2.74 \pm 0.55) \times 10^{-13}$ cm^3 $molec^{-1}$ s^{-1}

[a] See Reference 1
[b] See Reference 2
[c] See Reference 4
[d] See Reference 3

Table II. Acetylene statistical summary.

Run	Initial C_2H_6/C_2H_2 Ratio	Ethane pre-irradiation Analytical Relative s.d.	Acetylene pre-irradiation Analytical Relative s.d.	Regression Analysis: Slope $k_{OH-C_2H_2}/k_{OH-C_2H_6}$	Std. Error of Slope	Y Intercept (min^{-1})	Std. Error of Y Intercept	Is Intercept Significant?*	R^2 (%)
R-1	1:1	± 0.27%	± 0.36%	2.56	± 0.31	1.13 X 10^{-3}	±9.39 X 10^{-4}	No	97.1
L-1	1:1	± 0.21%	± 0.27%	3.21	± 0.21	1.70 X 10^{-4}	±2.41 X 10^{-4}	No	99.9
L-4	1:1	± 0.26%	± 0.52%	2.61	± 0.61	4.21 X 10^{-4}	±6.90 X 10^{-4}	No	90.0
L-5	1:1	± 0.30%	± 0.28%	1.80	± 0.16	7.13 X 10^{-4}	±1.86 X 10^{-4}	Yes	98.4
R-5	1:1	± 0.29%	± 0.26%	3.46	± 0.43	5.57 X 10^{-4}	±4.47 X 10^{-4}	No	97.0

* Is y intercept significantly distinguishable from the origin (Student's t-test at 5% significance level)? (The above statement applies to Tables II-VI).

Table III. Ethylene dichloride statistical summary.

Run	Initial $\frac{C_2H_6}{EDC}$ Ratio	Ethane pre-irradiation Analytical Relative s.d.	EDC pre-irradiation Analytical Relative s.d.	Regression Analysis: $\frac{\text{Slope } K_{OH-EDC}}{K_{OH-C_2H_6}}$	Std. Error of Slope	Y Intercept (min^{-1})	Std. Error of Y Intercept	Is Intercept Significant?*	R^2 (%)
R6A	1:1	± 1.1%	± 0.3%	0.783	±0.088	1.05×10^{-4}	$\pm 1.37 \times 10^{-4}$	No	96.4
L6A	1.1	± 1.1%	± 0.6%	0.959	±0.149	6.87×10^{-4}	$\pm 3.54 \times 10^{-4}$	No	83.8
R7	1:1	± 1.1%	± 0.2%	0.445	±0.035	7.29×10^{-5}	$\pm 7.93 \times 10^{-5}$	No	89.6
L7	1:1	± 2.1%	± 0.1%	0.367	±0.023	2.93×10^{-4}	$\pm 5.12 \times 10^{-5}$	Yes	94.0
R8	1:1	± 2.4%	± 0.2%	0.573	±0.040	3.51×10^{-4}	$\pm 1.27 \times 10^{-4}$	No	96.8
L8	1:1	± 0.7%	± 0.2%	0.419	±0.035	9.60×10^{-5}	$\pm 1.37 \times 10^{-4}$	No	96.0
R9	1:1	± 0.3%	± 0.2%	0.580	±0.060	1.84×10^{-4}	$\pm 1.30 \times 10^{-4}$	No	90.5
L9	1:1	± 0.2%	± 0.4%	0.536	±0.045	3.27×10^{-4}	$\pm 7.74 \times 10^{-5}$	Yes	95.4

Table IV. Ethylene dibromide statistical summary.

Run	Initial $\frac{C_2H_6}{EDB}$ Ratio	Ethane pre-irradiation Analytical Relative s.d.	EDB pre-irradiation Analytical Relative s.d.	Regression Analysis: Slope $\frac{K_{OH-EDB}}{K_{OH-C_2H_6}}$	Std. Error of Slope	Y Intercept (min^{-1})	Std. Error of Y Intercept	Is Intercept Significant?*	R^2 (%)
R13	1:1	±0.2%	±0.3%	0.845	±0.166	3.71×10^{-5}	1.60×10^{-4}	No	86.6
R14	1:1	±0.1%	±1.6%	1.50	±0.156	2.30×10^{-4}	5.44×10^{-4}	No	95.9
R15	1:1	±0.2%	±1.5%	1.23	±0.138	2.54×10^{-4}	1.97×10^{-4}	No	91.9
R17	1:1	±0.2%	±0.3%	0.548	±0.094	2.19×10^{-4}	2.06×10^{-4}	No	84.9
L17	1:1	±0.04%	±1.1%	0.690	±0.120	2.78×10^{-4}	1.34×10^{-4}	No	89.2
R18	1:1	±0.2%	±0.6%	1.27	±0.169	2.15×10^{-4}	1.70×10^{-4}	No	91.8

Table V. Para-dichlorobenzene statistical summary.

Run	Initial $\frac{C_2H_2}{PDB}$ Ratio	Ethane pre-irradiation Analytical Relative s.d.	PDB pre-irradiation Analytical Relative s.d.	Regression Analysis: Slope $\frac{K_{OH-PDB}}{K_{OH-C_2H_6}}$	Std. Error of Slope	Y Intercept (min^{-1})	Std. Error of Y Intercept	Is Intercept Significant?*	R^2 (%)
8/5 R1	1:1	±0.6%	±0.2%	1.40	±0.18	3.14×10^{-4}	2.60×10^{-4}	No	85.3
8/5 L1	1:1	±0.7%	±0.9%	1.23	±0.09	3.19×10^{-4}	1.61×10^{-4}	Yes	94.9
8/5 R2	1:1	±1.6%	±0.5%	1.37	±0.16	6.97×10^{-4}	2.53×10^{-4}	Yes	85.6
8/6 R1	1:1	±0.3%	±0.9%	1.23	±0.12	7.81×10^{-4}	2.23×10^{-4}	Yes	89.8
8/6 L1	1:1	±1.6%	±0.3%	1.17	±0.12	8.85×10^{-4}	2.94×10^{-4}	Yes	88.4
8/6 R3	1:1	±0.7%	±0.5%	1.38	±0.21	1.12×10^{-4}	5.23×10^{-4}	No	89.3
8/6 L3	1:1	±0.9%	±0.5%	1.66	±0.22	7.90×10^{-4}	7.11×10^{-4}	No	87.8
8/7 R1	1:1	±1.4%	±0.5%	1.89	±0.18	4.34×10^{-4}	3.04×10^{-4}	No	92.0
8/13 R1	16:1	±0.03%	±1.0%	1.94	±0.25	3.14×10^{-4}	1.55×10^{-4}	No	87.4
8/13 L1	16:1	±0.08%	±0.8%	1.90	±0.22	1.50×10^{-4}	1.62×10^{-4}	No	89.2
8/14 R1	16:1	±0.08%	±0.5%	1.63	±0.08	9.40×10^{-4}	1.37×10^{-4}	No	97.7
8/14 L1	16:1	±0.07%	±0.4%	1.68	±0.08	1.56×10^{-4}	2.09×10^{-4}	No	97.7

Table VI. Carbon disulfide statistical summary.

Run	Initial $\frac{C_2H_2}{CS_2}$ Ratio	Ethane pre-irradiation Analytical Relative s.d.	CS_2 pre-irradiation Analytical Relative s.d.	Regression Analysis: Slope $\frac{K_{OH-CS_2}}{K_{OH-C_2H_6}}$	Std. Error of Slope	Y Intercept (min^{-1})	Std. Error of Y Intercept	Is Intercept Significant?*	R^2 (%)
8/21 R1	1:1	±0.2%	±2.7%	12.3	±0.14	2.97×10^{-3}	5.74×10^{-4}	Yes	99.9
8/21 L1	1:1	±0.5%	±2.1%	9.42	±0.35	7.41×10^{-3}	1.08×10^{-3}	Yes	98.8
8/21 R2	1:1	±0.5%	±2.2%	10.7	±0.29	1.27×10^{-3}	3.49×10^{-3}	Yes	94.4
8/21 L2	1:1	±0.7%	±2.4%	9.41	±0.83	9.04×10^{-3}	2.16×10^{-3}	Yes	94.8
8/21 R3	1:1	±0.6%	±1.2%	7.28	±0.54	1.22×10^{-2}	1.59×10^{-3}	Yes	95.8
8/21 L3	1:1	±0.7%	±1.4%	13.3	±0.92	5.20×10^{-3}	1.90×10^{-3}	Yes	96.8
8/26 R1	16:1	±0.1%	±2.9%	15.2	±0.65	4.56×10^{-3}	1.37×10^{-3}	Yes	98.5
8/26 L1	16:1	±0.1%	±1.3%	14.8	±0.88	5.27×10^{-3}	1.42×10^{-3}	Yes	97.6
8/26 R2	8:1	±0.6%	±1.6%	9.05	±0.30	6.12×10^{-3}	6.77×10^{-4}	Yes	99.1
8/26 L2	8:1	±0.5%	±1.7%	8.79	±0.29	5.87×10^{-3}	8.17×10^{-4}	Yes	99.0

Table VI. Continued.

Run	Initial C_2H_2 / CS_2 Ratio	Ethane pre-irradiation Analytical Relative s.d.	CS_2 pre-irradiation Analytical Relative s.d.	Regression Analysis: Slope $K_{OH-CS_2}/K_{OH-C_2H_6}$	Std. Error of Slope	Y Intercept (min^{-1})	Std. Error of Y Intercept	Is Intercept Significant?*	R^2 (%)
8/26 R3	1:10	±2.7%	±2.1%	4.76	±0.37	1.11×10^{-2}	1.64×10^{-3}	Yes	97.7
8/26 L3	1:10	±2.1%	±0.8%	2.15	±0.22	2.02×10^{-2}	3.07×10^{-3}	Yes	93.3
8/27 R1	1:10	±3.1%	±1.2%	3.65	±0.25	1.30×10^{-2}	1.84×10^{-3}	Yes	96.3
8/27 L1	1:10	±3.0%	±0.4%	6.09	±0.63	9.28×10^{-3}	1.56×10^{-3}	Yes	93.1
8/28 R1	8:1	±0.4%	±1.1%	10.9	±0.32	5.87×10^{-3}	7.84×10^{-4}	Yes	99.3
8/28 L1	8:1	±0.4%	±1.9%	9.95	±0.32	8.63×10^{-3}	8.26×10^{-4}	Yes	99.1
8/29 R1	16:1	±0.5%	±0.8%	10.9	±0.23	6.78×10^{-3}	5.39×10^{-4}	Yes	99.6
8/29 L1	16:1	±0.4%	±1.4%	11.6	±0.26	5.16×10^{-3}	7.66×10^{-4}	Yes	99.6
8/29 R2	1:10	±2.5%	±0.8%	6.21	±0.61	6.66×10^{-3}	1.84×10^{-3}	Yes	93.8
8/29 L2	1:10	±2.0%	±1.1%	4.95	±0.25	8.49×10^{-3}	8.74×10^{-4}	Yes	98.3